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# Effect of Anthraquinones on Endwise Degradation of Hydrocellulose in Relation to Alkaline Pulping*

Irving I. Ziderman and Janine Belayche

Israel Fiber Institute, Ministry of Industry and Trade, PO Box 8001, 91 080 Jerusalem, Israel

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*SUMMARY*

*Anthraquinones promote early delignification and stabilisation of cellulose during alkaline pulping. Alkali-catalysed endwise depolymerisation of hydrocellulose was studied at 97°C under nitrogen. In the presence of sodium anthraquinone-2-sulphonate (AQS), the rates of both the chain-propagated unzipping reaction and the competing termination reaction were lowered. Since the former reaction was inhibited to a greater extent than the latter, less dissolution of cellulose occurred at this temperature. These findings are inconsistent with a mechanism that hypothesises coupling of an oxidative stabilisation of cellulosic chain-ends with chemical reduction of an anthraquinone catalyst.*

*The inhibitory action of AQS at 97°C is ascribed to its possible action of diminishing the degree of ionisation of cellulosic reducing chain-ends. As a possible mechanism for the accelerated dissolution of cellulose at pulping temperatures, it is suggested that anthraquinones promote intrachain scissions in cellulose, enhancing the dissolution of chain fragments before unzipping.*

*An anomalously high rate of peeling near neutrality is attributed to an uncatalysed reaction occurring simultaneously with the base-catalysed degradation.*

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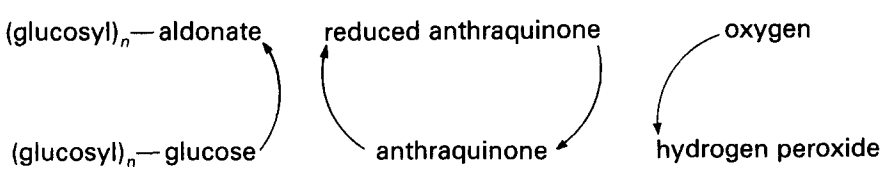
## INTRODUCTION

When added to alkaline pulping systems, anthraquinone (AQ) and its derivatives can act so as to facilitate early delignification in the cooking process and to stabilise polysaccharides against alkali-catalysed dissolution (Algar *et al.*, 1979). These beneficial effects may be enhanced by the synergistic action of oxygen, which has been depicted (Ruoho & Sjostrom, 1978; Algar *et al.*, 1979; Vuorinen & Sjostrom, 1982) as a coupled cyclic redox system (Scheme 1). The hypothesis requires that oxidation of cellulosic reducing termini to aldonate residues depletes the amount of active AQ, which is regenerated by aerobic oxidation of reduced AQ. (Reductive solubilisation of lignin is also considered to regenerate AQ (Dimmel, 1985).) In this way the cellulose chains are presumed to be protected against further degradation, resulting in an enhanced yield of cellulose.

The experimental approach used in our previous studies (Ziderman *et al.*, 1975; Lewin *et al.*, 1978; Ziderman & Belayche, 1978*a*,*b*, 1979; Ziderman & Weiss, 1979; Lewin & Ziderman, 1980; Ziderman, 1980*a*,*b*) of *beta*-eliminative endwise depolymerisation ('peeling', 'unzipping') of polysaccharides is herewith applied to determining the effect of anthraquinones on the alkali-catalysed stabilisation of hydrocellulose, in order to examine the validity of Scheme 1.

## EXPERIMENTAL

The substrate was an LODP-hydrocellulose of DP ~ 200, prepared as described previously (Ziderman & Belayche, 1978*a*). The anthra-




**Scheme 1.** Cyclic redox mechanism proposed for a carbohydrate and oxygen synergism in anthraquinone catalysis of pulping (according to Algar *et al.* (1979), Ruoho & Sjostrom (1978) and Dimmel (1985))

**TABLE 1**

Influence of Sodium Anthraquinone 2-Sulphonate (AQS) and Magnesium Chloride on Hydrocellulose Degradation (Hydrocellulose (100 mg) in 0·1 M Sodium Hydroxide (10 $cm^3$) Stirred for 2 h at 97°C)

| *Experiment No.* | *AQS (g litre$^{-1}$)* | *Loss-in-weight (mg) of hydrocellulose under atmosphere of:* | | | |
|---|---|---|---|---|---|
| | | *Air* | | *Nitrogen* | |
| | | *Control (no AQS)* | *Result with AQS* | *Control (no AQS)* | *Result with AQS* |
| 1 | 0·1 | 23·9, 24·1 | 23·3, 20·2 | 23·2, 24·8, 23·5[e] | 23·3, 24·0, 22·6[e] |
| 2 | 0·3 | 23·9, 24·1 | 22·3, 21·15 | 23·2, 24·8, 23·5[e] | 21·25, 22·2, 23·3[e] |
| 3 | 0·5[a] | 23·0 | 22·8, 22·3, 22·0 | ND | ND |
| 4 | 1 | 23·9, 24·1 | 15·7 | 23·2, 24·8, 23·5[e] | 21·5, 20, 19·8[e] |
| 5 | 1 | 25·1, 24·6 | 15·5, 19·2, 18 | 23·2, 23·1 | 23·0, 19·9, 20·4 |
| 6 | 1[a] | 23·2 | 13·6, 14·6 | ND | ND |
| 7 | 2 | 25·1, 24·6 | 17·4, 19·2 | 23·2, 23·1 | 13·8, 15·5 |
| 8 | 2 | ND | ND | 25·1, 24·6 | 24·5, 20 |
| 9 | 2[a] | 23·2 | 17·3, 13·7 | ND | ND |
| 10 | 5 | 24·0 | 10·2. 10·0, 4·5 | 23·9 | 11·2, 21·5, 8·8 |
| 11 | 5 | 19·9, 21·1 | 11·7, 9·5 | 24·0 | 9·4 |
| 12 | 5[b] | 21·0, 23[c] | 16·7, 13·8 | ND | ND |
| 13 | 10 | 19·9, 21·1 | 10·0, 7·0, 10·7 | ND | ND |
| 14 | 10[b] | 21·0[d] | 13·4 | ND | ND |

[a] AQ instead of AQS.
[b] 1 g litre$^{-1}$ magnesium chloride.
[c] Without magnesium chloride, 23 mg.
[d] Without magnesium chloride, 21·1 mg.
[e] No stirring.
ND = not determined.

quinone-2-sulphonic acid sodium salt monohydrate (AQS) was a 'pro analysi' grade Merck product. Hydrocellulose (100 mg) was magnetically stirred with 0·1 M sodium hydroxide (10 $cm^3$) in a sealed tube placed in a boiling water bath (97°C) for 2 h with increasing concentrations of AQS under air or nitrogen, as detailed in Table 1, and the loss in weight of the hydrocellulose was measured.

Since the extent of reaction under nitrogen was unaltered when stirring was omitted (experiment No. 4 cf. No. 5), it was justified to compare data obtained with and without stirring. In the absence of AQS, the presence of air did not decrease polysaccharide degradation, so no conversion of reducing chain ends to aldonate occurred due to reaction with atmospheric oxygen. Thus, it was reasonable to assume that stabilisation occurring in the presence of both AQS and air was solely due to the former additive.

Reaction kinetics were similarly determined under nitrogen as previously described (Ziderman & Belayche, 1978*a*). Initial pH levels as measured at ambient temperature were 11 and 13, which correspond (Ziderman & Belayche, 1978*a*) to 10 and 10·6, respectively, at a reaction temperature of 97°C. As previously described (Ziderman & Belayche, 1978*a*), the gravimetric degradation data yielded two apparent first-order rate constants, $k_1$ for hydrocellulose endwise depolymerisation and $k_t$ for termination reactions (chain stabilisation), as well as the asymptotic extent of degradation $L_\infty$ ($= \nu/DP$) and the alkali-degradable chain length $\nu$ ($= k_1/k_t$). The rate constants are defined in the theory of Haas *et al.* (1967) as follows:

$$\text{rate of chain peeling} = k_1[G_r]$$

$$\text{rate of chain termination} = k_t[G_r]$$

where $[G_r]$ is the mole fraction of reducing endgroups that are available for reaction.

## RESULTS

### Comparison of AQ with AQS

In aerobic systems, the effect of AQ in inhibiting hydrocellulose degradation (experiments No. 3, 6 and 9; Table 1) was similar to that of AQS at the same concentration. The enhanced effectiveness of AQS reported elsewhere (Carlson & Samuelson, 1979, 1981;

Vuorinen & Sjostrom, 1982) may perhaps be attributed to differences in the proportion of reactants, reaction conditions and additives employed.

**Concentration dependence** (Table 1)

The protective action of AQS was concentration dependent as previously reported (Heikkile & Sjostrom, 1975), increasing in the present system to a maximal level at 5 g litre$^{-1}$. In the presence of atmospheric oxygen, the activity of AQS was enhanced, so that an initial protective effect was obtained at a lower AQS level (1 g litre$^{-1}$) than under nitrogen ([AQS] $\geqslant$ 2 g litre$^{-1}$).

**Effect of magnesium salts** (Table 1)

In an aerobic system, magnesium chloride diminished the stabilising influence of AQS on hydrocellulose, which is tentatively ascribed to possible precipitation of a magnesium salt of AQS. The *protective* action previously reported for magnesium compounds was ascribed (Basta & Samuelson, 1979; Isbell *et al.*, 1981) to scavenging of trace metals, and would accordingly be inoperative in the present system, from which trace metals had been removed from the substrate during purification.

**Kinetic results**

The data in Table 2 show that AQS reduced the rates of both peeling and termination processes. Since *fewer* chain terminations took place

**TABLE 2**

Influence of Sodium Anthraquinone 2-Sulphonate (AQS) on the Kinetics for the Alkali-Catalysed Degradation of Hydrocellulose[a]

| *AQS* (*g litre*$^{-1}$) | *pH* | | $L_\infty$ | $\nu$ | $k_1$ ($h^{-1} \times 10^2$) | $k_1$ ($h^{-1}$) |
|---|---|---|---|---|---|---|
| | *25°C* | *97°C* | | | | |
| 0 | 11·0 | 10·0 | 0·48 | 103 | 19 | 20 |
| 5 | 11·0 | 10·0 | 0·24 | 52 | 9·0 | 4·7 |
| 0 | 13·0 | 10·6 | 0·40 | 86 | 47 | 40 |
| 5 | 13·0 | 10·6 | 0·18 | 40 | 26 | 10 |

[a] Hydrocellulose (100 mg) stirred in 10 cm$^3$ alkaline medium under nitrogen at 97°C.

in the presence of AQS, it is clear that hydrocellulose was not stabilised by additional reducing chain termini being oxidised to alkali-stable aldonate residues by the AQS. The dissolution of hydrocellulose was curtailed (lower $L_\infty$ value) because the termination rate was reduced much less than the peeling rate.

## DISCUSSION

### Diminished termination rate

On alkali treatment of celluloses in the presence of anthraquinones, there is an increase in carboxylate endgroup content (Heikkile & Sjostrom, 1975; Lowendahl & Samuelson, 1977; Ruoho & Sjostrom, 1978). Since AQS preferentially slows down the rate of unzipping ($k_1$) to a greater extent than the rate of competing termination reactions ($k_t$, Table 2), more reducing endgroups will be converted to saccharinate residues in the alkali-catalysed termination reaction, resulting in the reported increase in carboxylate content. The kinetic results accordingly indicated that the mechanism does not involve an *acceleration* of chain terminations, such as oxidation of additional reducing ends to aldonate residues by anthraquinones.

Because of the decreased value for the ratio $k_1/k_t$ in the presence of AQS, the asymptotic weight loss of the polysaccharide $L_\infty$ is smaller (Table 2). AQS is more effective in stabilising cellulose than is AQ (Ruoho & Sjostrom, 1978). Analogous protective effects are also exhibited in other systems, particularly in the pH-profiles of $k_1$ and $k_t$ (Ziderman, 1980*b*) and in the effects of cationic valency on alkaline degradation of pectin (Keijbets & Pilnik, 1974) and hydrocellulose (Ziderman, 1980*b*). In each of these cases, a stabilisation effect is attributed essentially to a lowering of the *effective* alkalinity. Decreased hydroxide ion activity at the reaction site would diminish the concentration of ionised endgroups, thereby causing a decrease in reaction rates $k_1$ and $k_t$.

Similarly, in the case of AQS, the highly dissociated salt may becomed associated with the polysaccharide via its sodium cations, and thereby enhance the weakly negative electrostatic charge of the polymer surface by virtue of the highly charged sulphonate anions. The approach of catalysing hydroxide anions will thus be retarded,

decreasing the effective alkalinity in the vicinity of the reducing ends, which will consequently be less ionised.

The enhanced sensitivity of $k_1$ to hydroxide ion activity over that of $k_t$ may be explained by the necessary dependence of chain termination, through saccharide production, on the formation of a terminal dianionic intermediate due to ionisation of a second carbohydrate hydroxyl function (Lai & Sarkanen, 1969; Ziderman, 1980*b*).

## Action of anthraquinones in pulping

The kinetic results (Table 2) indicate that reduction of AQS is not coupled with an oxidation of polymer endgroups to aldonate residues, as depicted in Scheme 1. In any case, aldonate endgroups are labile at pulping temperatures (Vuorinen & Sjostrom, 1982), and would not stabilise polymeric chains. Consequently, the synergistic action of anthraquinones and carbohydrates in aerobic pulping requires an alternative explanation.

In addition to propagative scission of glucosidic linkages at reducing chain-ends by peeling, intrachain degradation may occur at pulping temperatures (*c.* 170°C) by alkali-catalysed hydrolysis (Lai & Sarkanen, 1967; Kubes *et al.*, 1983) and/or by oxidative mechanisms (Meller, 1960). Newly generated reducing ends of these cellulose chain fragments provide additional sites for the consecutive initiation of peeling. (In the present study, this situation was avoided (Lai & Sarkanen, 1967) by performing anaerobic degradations at 97°C rather than at a pulping temperature, thereby evading complications in kinetic interpretation of the data.)

It is accordingly proposed that, in the presence of anthraquinones, the major pathway of polysaccharide dissolution at pulping temperatures may shift from endwise peeling to AQ-catalysed oxidative intrachain scission. This explanation is supported by the enhanced rate at which the intrinsic viscosity drops during aerobic cooking of wood meal with anthraquinones (Carlson & Samuelson, 1981); in the absence of oxygen, pulp viscosity is unaffected by reducing additives (Kubes *et al.*, 1983).

AQ would probably act through oxidation of 2-OH/3-OH or 6-OH to a carbonyl function, forming, respectively, keto-cellulose or *aldehydo*-cellulose, in which chain rupture occurs by *beta*-eliminate cleavage between C-1 and 1-O (Ziderman, 1980*a*) or

between C-4 and 4-O (Meller, 1960), respectively. The oxidation may be mediated by the action of hydrogen peroxide that is formed *in situ* when AQ is oxidised by molecular oxygen (Scheme 1).

Dissolution of short-chain fragments that are formed in this manner could account for an accelerated loss of cellulose during pulping, and *their* oxidation in solution rather than that of fibre chain termini would be responsible for regenerating AQ to its reduced state (cf. Scheme 1).

Quantitative analyses of pulp composition (Table 3) correspond to this mechanism. AQ evidently acts so as to attain a similar cellulose yield as in the absence of AQ but in a shorter time and at a lower initial alkalinity (Vanderhoek, 1981). The same alkali consumption that occurs both with and without AQ (Vanderhoek, 1981) confirms that, in both cases, a similar amount of cellulose has been degraded to acidic fragments (saccharinates) by unzipping.

The data of Table 3 indicate that the rate of cellulose dissolution during soda delignification has been accelerated by AQ. While this effect has been ascribed above to a putative enhancement of oxidative chain rupture, one may not exclude a possible influence of the more rapid dissolution of lignin that is occurring. In any case, if the reduction of AQ, as depicted in Scheme 1, is considered to be coupled mechanistically to oxidation of dissolved carbohydrate fragments rather than of pulp cellulose fibres, then no enhanced stabilisation of cellulosic fibres is required to occur.

## Peeling of hydrocellulose in neutral solution

In a recent study of the endwise degradation of hydrocellulose at 140°C, Chiang & Sarkanen (1985) found that, as the alkalinity is decreased below pH 11, the rate of peeling declines less than the values predicted solely on the basis of endgroup ionisation, as expressed by the hypothetical eqn (1):

$$\text{rate of propagation} = k_p \times [\text{end group anion}] \qquad (1)$$

In fact, a significant rate of peeling was measured even at pH 7. The authors were unable to explain this anomalous observation.

Hydrocellulose is known (Ziderman & Belayche, 1978*a*) to behave in a similar fashion when degraded at 98°C. Below a pH of *c.* 8·5, the $k_p$ observed at this temperature was independent of alkalinity, and was

**TABLE 3**
Influence of Anthraquinone on Composition of Pine Wood Pulps

| *Process* | *Total yield* (%) | *Composition* (% *of raw wood*) | | | |
|---|---|---|---|---|---|
| | | *Lignin* | *Extractables* | *Carbohydrates* | |
| | | | | *Hemicelluloses* | *Cellulose* |
| *P. radiata*[a] | | | | | |
| Raw wood | — | 27 | 3 | 25 | 45 |
| Soda/AQ[b] | 47 | 2 | 0 | 10 | 35 |
| Soda | 55 | 10 | 0 | 45 | |
| Kraft | 48 | 2·5 | 0 | 45·5 | |
| Kraft/AQ[b] | 49–50 | 2·5 | 0 | 46·5–47·5 | |
| *P. silvestris*[c] | | | | | |
| Raw wood | — | 26·4 | — | 25·5 | 39·6 |
| Soda/AQ[d] | 53·8 | 5·4 | — | 9·6 | 38·7 |
| Soda[e] | 49·2 | 4·7 | — | 7·1 | 37·4 |

[a] Data from Vanderhoek (1981).
[b] 0·1% Anthraquinone on wood.
[c] Data from Kosikova *et al.* (1980): 3·5 liquor/wood, 120 min. to maximum temperature 170°C.
[d] 1·38 M Sodium hydroxide, 0·4% AQ on wood, 30 min at 170°C.
[e] 1·75 M Sodium hydroxide, 90 min at 170°C.

accordingly considered to represent the rate constant for the uncatalysed reaction ($k_0$), in accordance with reaction (2):

$$\text{cellulose-}G_rH \xrightarrow{k_0} \text{products} \qquad (2)$$

where $G_rH$ signifies an un-ionised reducing endgroup. Above pH 9·8, $k_p$ increased with alkalinity in accordance with a specific hydroxide-ion catalytic mechanism, thereby providing experimental evidence for a dependence on endgroup ionisation, as required in eqn (1).

Accordingly, it was concluded (Ziderman & Belayche, 1978*a*) that unzipping of hydrocellulose at 98°C may be described by expression (3):

$$\text{rate of propagation} = (k_0 + k_{OH^-}[OH^-])[G_rH] \qquad (3)$$

where $k_{OH^-}$ is the catalytic coefficient. The specific rate constant for the catalysed reaction $k'$ is as defined in reaction (4):

$$\text{cellulose–}G_r^- \xrightarrow{k'} \text{products} \tag{4}$$

and was obtained using eqn (5):

$$k' = k_{OH^-} . K_h \tag{5}$$

where $K_h$ is the hydrolysis constant for $G_rH$. Calculation showed that, at 98°C, the uncatalysed reaction undergoes acceleration by a factor of 340 ( $= k'/k_0$) due to base catalysis.

The same explanation will probably account for the findings of Chiang & Sarkanen (1985).

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## REFERENCES

Algar, W. H., Farrington, A., Jessup, B., Nelson, P. F. & Vanderhoek, N. (1979). *Appita* **33**, 33.
Basta, J. & Samuelson, O. (1979). *Svensk Papperstidn.* **82**, 337.
Carlson, U. & Samuelson, O. (1979). *Svensk Papperstidn.* **82**, 48.
Carlson, U. & Samuelson, O. (1981). *J. Wood Chem. Technol.* **1**, 43.
Chiang, V. L. & Sarkanen, K. V. (1985). *J. Wood Chem. Technol.* **5**., 203.
Dimmel, D. R. (1985). *J. Wood Chem. Technol.* **5**, 1.
Haas, D. W., Hrutfiord, B. F. & Sarkanen, K. V. (1967). *J. Appl. Polymer Sci.* **11**, 587.
Heikkile, H. & Sjostrom, E. (1975). *Cell. Chem. Technol.* **9**, 3.
Isbell, H. S., Frush, H. L., Naves, R. & Soontracharoen, P. (1981). *Carbohyd. Res.* **90**, 111.
Keijbets, M. J. H. & Pilnik, W. (1974). *Carbohyd. Res.* **33**, 359.
Kosikova, B., Janson, J., Pekkala, O. & Sargfors, P. (1980). *Paperi ja Puu-Papper o. Tra* **62**, 229.
Kubes, G. J., Fleming, B. I., MacLoed, J. M. & Bolker, H. I. (1983). *J. Wood Chem. Technol.* **3**, 313.
Lai, Y. & Sarkanen, K. V. (1967). *Cell. Chem. Technol.* **1**, 517.

Lai, Y. & Sarkanen, K. V. (1969). *J. Polymer Sci.: Part C* **28**, 15.
Lewin, M. & Ziderman, I. (1980). *Cell. Chem. Technol.* **14**, 743.
Lewin, M., Ziderman, I., Weiss, N., Basch, A. & Ettinger, A. (1978). *Carbohyd. Res.* **62**, 393.
Lowendahl, L. & Samuelson, O. (1977). *Svensk Papperstidn.* **80**, 549.
Meller, A. (1960). *Holzforsch.* **14**, 129.
Ruoho, K. & Sjostrom, E. (1978). *Tappi* **61**, 87.
Vanderhoek, N. (1981). Paper presented at Israel Fiber Institute, Jerusalem.
Vuorinen, T. & Sjostrom, E. (1982). *J. Wood Chem. Technol.* **2**, 129.
Ziderman, I. (1980*a*). *Carbohyd. Res.* **81**, 196.
Ziderman, I. (1980*b*). *Cell. Chem. Technol.* **14**, 703.
Ziderman, I. & Belayche, J. (1978*a*). *J. Appl. Polymer Sci.* **22**, 711.
Ziderman, I. & Belayche, J. (1978*b*). *J. Appl. Polymer Sci.* **22**, 1151.
Ziderman, I. & Belayche, J. (1979). *J. Appl. Polymer Sci.* **23**, 3427.
Ziderman, I. & Weiss, N. (1979). *J. Appl. Polymer Sci.* **23**, 1883.
Ziderman, I., Belayche, J., Basch, A. & Lewin, M. (1975). *Carbohyd. Res.* **43**, 255.